Julian Heicklen

ATMOSPHERIC CHEMISTRY
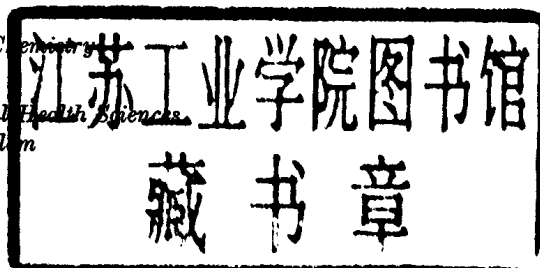
Atmospheric Chemistry

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ATMOSPHERIC CHEMISTRY

To the future:
Judykins, Allie Pallie, and Debchick
And to those who made it possible:
my wife, Susan, and our parents

If I forget thee, O Jerusalem
Let my right hand forget its cunning
Let my tongue cleave to the roof of my mouth

PREFACE

The last comprehensive book on air pollution chemistry was the truly excellent monograph by Philip Leighton entitled "Photochemistry of Air Pollution," which appeared in 1961. Unfortunately it is now hopelessly out of date. Although a number of books have appeared recently on various aspects of upper atmospheric chemistry, they are not particularly comprehensive. In some cases they are restricted to the stratosphere or the ionosphere, or their emphasis is more on the meteorology or physics of the upper atmosphere. None of them relates tropospheric events with those in the upper atmosphere.

Over the past decade our knowledge of atmospheric chemistry has increased tremendously as a result of atmospheric observations and monitoring, laboratory determinations of reaction mechanisms and rates, and atmospheric modeling studies. The recently concluded Climatic Impact Assessment Program of the U.S. Department of Transportation has greatly increased our knowledge of the stratosphere. It seemed appropriate to attempt to correlate this material in order to obtain a comprehensive picture of the atmospheric chemical cycles. No attempt has been made to include details of engineering, meteorology, or health effects, though these have been discussed and included in an elementary manner when appropriate. The aim is to present the main features of the chemistry of the atmosphere in a manner that will prove useful to graduate students and to scientists in the field who wish to study atmospheric chemistry.

ACKNOWLEDGMENTS

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CONTENTS

Chapter I

STRUCTURE OF THE ATMOSPHERE

The earth's atmosphere is necessary to support all of life. Its major constituents are nitrogen and oxygen, but many other species are also present, thus making it a complex and interesting chemical system. The other compounds present include all the known ones composed of H, N, and O (except for N_2H_4). In addition the natural atmosphere contains CO, CO_2, CH_4, and CH_2O. Various parts of the upper atmosphere contain ions and electronically excited species. When other species are introduced through meteor entry, volcanic eruption, urban air pollution, or aircraft exhaust, then atmospheric chemistry becomes so complex that all of its details have not been understood even in simplified schemes. In this book we shall attempt to present what is known about the composition and chemistry of the atmosphere.

PHYSICAL CHARACTERISTICS

The structure of the atmosphere has been considered in a number of ways, often by its physical properties.

Temperature

The most common division of the atmosphere has been by its temperature profile, as shown in Fig. I-1. At the surface of the earth, there is a large variation in temperature, but typically a daytime midlatitude temperature is about 290°K. As the altitude increases the temperature drops to a minimum value of about 210°K at about 15 km in the midlatitude regions. Specifically, at the equator the minimum temperature is 190°K at 17 km. At the poles the minimum temperature of 200°K is reached at about 8 km.
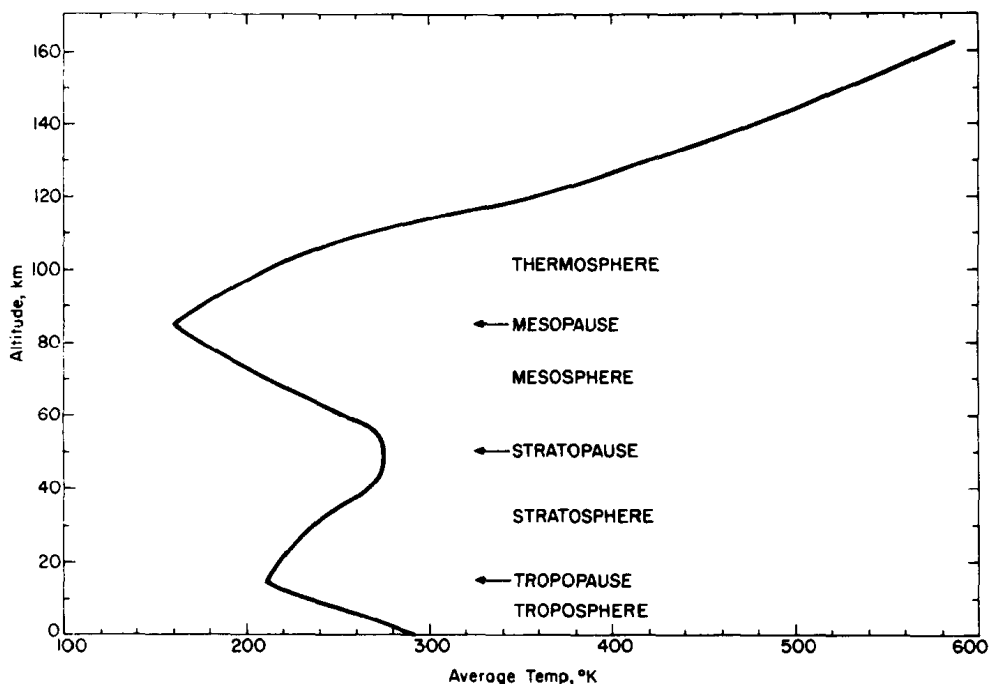
Fig. I-1. Plot of average temperature versus altitude.

This region of declining temperature with increasing altitude near the earth's surface is called the troposphere, and the region of the temperature minimum the tropopause.

Above the tropopause is the stratosphere, a region where the temperature rises with altitude until a maximum value of about 273°K is reached at 50 km at the equator and midlatitude regions. However near the poles there is a wide temperature variation. At Barrow, Alaska (71° N), the temperature maximum at 50 km varies from <240°K in the winter to >280°K in the summer (Theon and Smith, 1971). The altitude of maximum temperature is called the stratopause. Further increases in altitude are then accompanied by a falling temperature through the region known as the mesosphere until a minimum is reached again at 85 km (the mesopause). The minimum value at the mesopause is about 190–200°K at the equator, 170–210°K at midlatitudes, and 130–230°K at high latitudes (Theon and Smith, 1971). The higher end of the range is reached in summer, and the lower end in winter. Further increases in altitude lead to a rapid rise in temperature (5°/km at 150 km) through the region known as the thermosphere, which extends well beyond 150 km.

The reasons for the interesting temperature profile are related to the chemical composition of the atmosphere. At high altitudes, the sun's radiation in the vacuum ultraviolet region of the spectrum (<2000 Å) is being absorbed by atomic and molecular oxygen and nitrogen. This energy becomes heat and high temperatures result. As the altitude drops the vacuum ultraviolet radiation density drops because of this absorption and the temperature falls. However, at about 85 km and below another chemical species, ozone, becomes important. Its concentration increases as the altitude falls, reaching a maximum at about 25 km. It absorbs radiation between 2000 and 3000 Å, i.e., radiation that has not been removed at higher altitudes. Thus this absorption leads to heating, accounting for the mesosphere. At the stratopause ($\sim$50 km), enough of this radiation has been removed, so that the solar heating becomes less and less effective for further decreases in altitude, even though the ozone concentration is still rising. The increase in temperature below the tropopause to the earth's surface is due to absorption of the visible and near ultraviolet radiation (>3000 Å) at the earth's surface and reradiation.

Diffusion

Another way of structuring the earth's surface is through its diffusion characteristics. Since diffusion is a temperature- and pressure-dependent function it also changes with altitude. Table I-1 lists the average temperature, pressure, and density as a function of altitude. It can be seen that, although the temperature fluctuates up and down as the altitude is changed, the pressure and density fall continuously as the altitude increases.

Diffusion can arise from two sources. One of these is molecular diffusion, i.e., a molecule moves through the gas because of its individual velocity. This type of diffusion is readily computed from gas kinetic theory and varies inversely with the pressure. The computed value of the molecular diffusion coefficient for N_2 moving through N_2 is shown in Fig. I-2. This type of diffusion is unimportant at low altitudes, but increases in importance as the altitude is raised and the pressure drops. It becomes the dominant diffusion term above about 115 km.

At lower altitudes, the dominant diffusion term is that due to turbulent mixing (convection), referred to as eddy diffusion. The estimated eddy diffusion coefficients for vertical transport also are shown in Fig. I-2. There is considerable uncertainty in their values, so that a range of values is shown, as computed from different models (Hays and Olivero, 1970).

In the troposphere (<15 km) and mesosphere (50–85 km), the eddy diffusion coefficients are larger than in the stratosphere (15–50 km). This is because the temperature drops with rising altitude in the troposphere

TABLE I-1

Average Atmospheric Parameters at Various Altitudes

Altitude (km)	Temperature (°K)	Pressure (Torr)	Density (particles/cm³)
0	291	7.6×10^2	2.5×10^{19}
5	266	3.7×10^2	1.3×10^{19}
10	231	1.8×10^2	7.7×10^{18}
15	211	8.5×10	3.9×10^{18}
20	219	3.9×10	1.7×10^{18}
25	227	1.8×10	7.7×10^{17}
30	235	8.6	3.6×10^{17}
35	252	4.3	1.7×10^{17}
40	268	2.2	8.1×10^{16}
45	274	1.2	4.3×10^{16}
50	274	6.6×10^{-1}	2.3×10^{16}
55	273	3.6×10^{-1}	1.3×10^{16}
60	253	1.9×10^{-1}	7.2×10^{15}
65	232	9.4×10^{-2}	3.9×10^{15}
70	211	4.4×10^{-2}	2.0×10^{15}
75	194	1.9×10^{-2}	9.6×10^{14}
80	177	7.9×10^{-3}	4.2×10^{14}
85	160	2.9×10^{-3}	1.9×10^{14}
90	176	1.4×10^{-3}	7.6×10^{13}
95	193	6.4×10^{-4}	3.2×10^{13}
100	210	2.4×10^{-4}	1.1×10^{13}
105	235	—	—
110	265	5.8×10^{-5}	2.1×10^{12}
115	310	—	—
120	355	2.0×10^{-5}	5.4×10^{11}
125	390	—	—
130	420	8.5×10^{-6}	1.95×10^{11}
135	450	—	—
140	480	4.6×10^{-6}	9.3×10^{10}
145	503	—	—
150	530	2.7×10^{-6}	4.9×10^{10}
155	550	—	—
160	575	1.7×10^{-6}	2.9×10^{10}

and mesosphere; the warmer air at the bottom of these regions rises easily. The stratosphere is a region where the temperature profile rises with altitude, and the tendency for vertical mixing is very small. Thus the stratosphere is the most stable (to mixing) region of the atmosphere.

By the same argument, one might expect that the eddy diffusion coefficient would again be reduced in the thermosphere, where the temperature
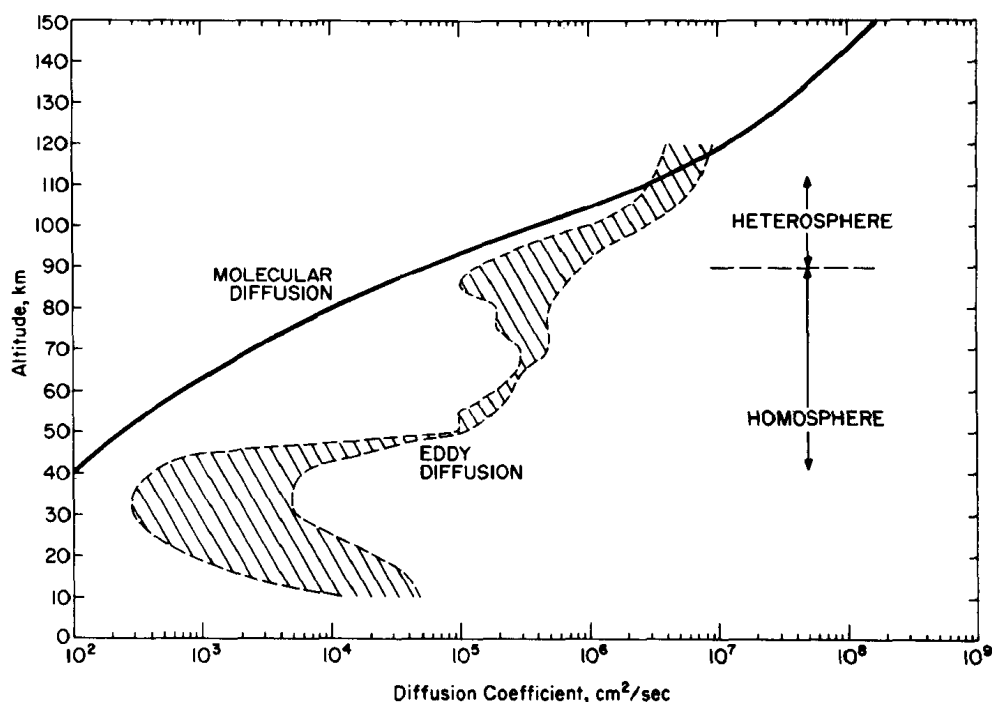
Fig. I-2. Semilog plots of diffusion coefficients versus altitude. Because of the uncertainty in the eddy diffusion coefficient, a range of values is shown. The molecular diffusion curve is for N_2 in N_2.

is again rising with altitude. However, in the region from 85 to 120 km, there are strong vertical shears in the horizontal wind induced by upward propagating gravity waves and atmospheric tides. These wind shears induce turbulence even in regions of increasing temperature so that vertical mixing by eddy diffusion continues to increase with altitude until about 120 km. Above this altitude, eddy diffusion becomes meaningless, because the molecular diffusion is more important, and turbulence is not a distinguishable phenomenon.

The region of the atmosphere below 90 km has a nearly constant mean molecular mass, and is therefore called the homosphere. The composition is essentially 78% N_2, 21% O_2, and 1% Ar. In this region molecular diffusion is negligible compared to eddy diffusion. Above 90 km, the O_2 and N_2 can be dissociated to a significant extent, and the mean mass of the species drops as the altitude increases. In this region, known as the heterosphere, molecular diffusion is significant and, above ~115 km, the dominant diffusion process.